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ELECTRODE POTENTIAL OF NICKEL. PART I. MEASUREMENTS IN AN ATMOSPHERE OF HYDROGEN WITH REDUCED NICKEL POWDER.

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Although much has been written concerning the phenomena which are observed when nickel is involved in the electrolytic process, only a small amount of work has been published dealing with the direct determination of the electrode potential of nickel, and as the measured values of the electrode potential, as shown in Table 1, can by no means be said to be in agreement with one another, it is desirable to find some means of making a reliable nickel electrode which will give a reproducible, constant, and reversible potential.

TABLE 1.

The equilibrium potential of nickel in N/1 $NiSO_4$ solution.

B. Neumann, *Z. physik. Chem.*, 14 (1894), 215.	−0.255 volt
A. Siemens, *Z. anorg. Chem.*, 41 (1904), 249.	−0.221 „
H. Euler, *Z. anorg. Chem.*, 41 (1904), 93.	−0.183 „
W. Muthmann & F. Fraunberger, *Sitz. Bayer. Akad. Wiss.*, 34 (1904), 201.	−0.597 „
E. P. Schoch, *Amer. Chem. Journ.*, 41 (1909), 208.	−0.197 „
A. Schweitzer, *Z. Elektrochem.*, 15 (1909), 607.	−0.33 „
R. Schildbach, *Z. Elektrochem.*, 16 (1910), 967.	−0.25 „
A. Smits and Lobry de Bruyn, *Proc. Acad. Sci. Amsterdam*, 20 (1918), 394.	−0.197 „
The writer (calculated* from the normal electrode potential)	−0.276 „

* The other necessary data for this calculation were obtained from the writer's paper on the conductance of nickel sulphate sulution (this journal, 3 (1928), 47). The value of relative viscosity was obtained by assuming that its deviation from unit is approximately proportional to the concentration.

A close study of previous works on the nickel electrode potential, above cited, especially those by Schoch, Schildbach and Schweitzer and the works of Richards and Behr[1], Foerster[2] and Schildbach on the electrode potentials of the metals of the same group, i.e. iron and cobalt, show why the observed values of the electrode potential of nickel differ one from another.

(1) Richards and Behr, *Z. physik. Chem.*, 58 (1907), 301.
(2) Foerster, *Abhandl. Deut. Bunsen Gesellsch.*, No. 2 (1909).

The potential of nickel electrode changes very considerably with the mode of preparation, previous treatment, and the state of the electrode, which causes can be divided into two factors, i.e. physical and chemical. Schoch and Schweitzer obtained higher and more constant values of the electrode potential with powdered nickel than with solid. It is well known that this physical factor has a similar effect on the electrode potential in the cases of other metals also and that the finely divided state of the metal is more favourable for the reproducibility and the constancy of the electrode. It has been suggested by G. N. Lewis[1] that the lack of reproducibility in the case of solid metal is due to the highly strained condition or unstable physical state of the metal whether it be produced by rolling or by electrolysis. Then it is natural that there is no agreement even in the measurements of these two investigators both working with powder but from different sources. Turning to the chemical factor, it is an important fact, observed definitely by Schoch, that the potential is diminished by the presence of air and increased by the introduction of hydrogen into the cell. As this effect of oxygen is rather specific to metals of the iron group and to chromium, it must have a close relation with the phenomena of passivity. It is therefore necessary to avoid any contact with oxygen by both the electrode and the solution, for the purpose of obtaining the true potential of active nickel. In this respect the above three investigators were careful in preparing the electrolyte and they boiled the solution before introducing it into the cell. On the other hand, in their mode of preparation of the electrode there still remains a little which leads us to suspect that they did not measure the true potential of active nickel. All the nickel used were those which had been kept in air and even the reduced nickel powder used by Schoch must have had the probable chance of coming into contact with the air while moving from the furnace into the cell. Schweitzer in all of his experiments polarised the electrodes cathodically in the cell with a solution of caustic potash to reduce any trace of oxide on the surface and, after washing, filled the cell with the electrolyte entirely in the absence of air. Schoch also once used the polarised electrode. As for the results with such electrodes, full discussion will be made later together with the results of the writer's experiments with polarised electrodes.

The writer obtained a reproducible and fairly constant electrode which gave a reversible electrode potential of active nickel by using powder electrode reduced in the cell, and using an apparatus which allows the cell to be filled in an atmosphere of hydrogen. But, as Schoch, and Richards and Behr reported that the occluded hydrogen raises the potential of nickel

(1) Lewis and Randall, "Thermodynamics," (1923), p. 388.

or iron, similar experiments were made in an atmosphere of nitrogen and in an atmosphere of a mixture of nitrogen and hydrogen, the results of which experiments might lead to the conclusion that the occluded hydrogen has no effect in the case of nickel. The report on those latter experiments will be made in the second part of this paper which will be published in the very near future.

Materials. *Water.*—Throughout the experiment conductivity water which had a specific conductance of less than 1.2×10^{-6} was used.

Nickel Oxide.—The nickel oxide was prepared by precipitation from a hot (90°C.) dilute (1%) solution of Kahlbaum's cobalt-free nickel nitrate with redistilled ammonia, washed thoroughly by decantation and filtration and dried. The dried material was crushed in an agate mortar into powder and then heated, to remove any nitrate that remained, in a furnace by passing an air current for about six hours at 600° to 700°C. and for one additional hour at 700° to 800°C.

Electrolyte.—In the experiments, nickel sulphate was employed as the electrolyte, because uni-bivalent salt is liable to form intermediate ions, and also for the convenience of comparing the result of these measurements with those of the previous investigators. Kahlbaum's cobalt-free sulphate was recrystallized twice from conductivity water and used. The concentrations were determined by electrolysis for nickel[1].

Apparatus and General Procedure. As was stated above the half cell for the nickel electrode was so designed as to allow the reducing of powdered

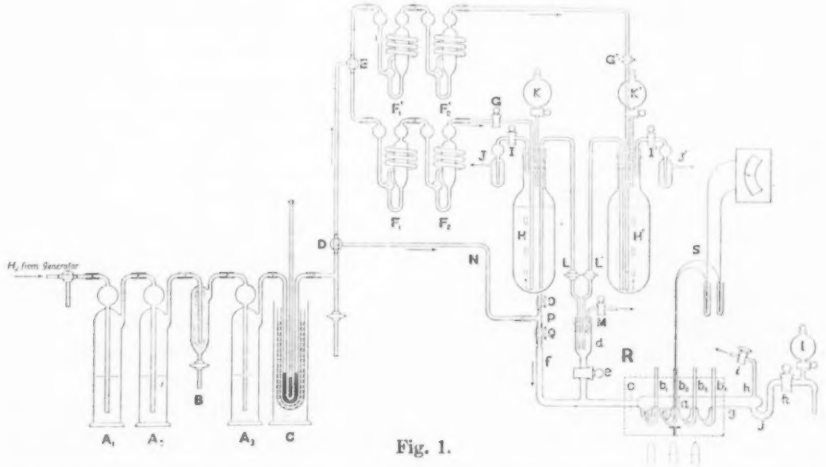

Fig. 1.

(1) Treadwell-Hall, "Analytical Chemistry" II, (1915), p. 136.

nickel oxide with hydrogen directly in the cell, and if desired, of permitting prolonged evacuation at high temperature to remove hydrogen occluded in the nickel electrode. And the apparatus was so arranged that the electrolyte could be transferred into the cell without contact with air.

Fig. 1 shows the whole arrangement of the apparatus and the half cell. R is the electrode vessel which is made of glass, having four separate electrode compartments b_1, b_2, b_3, b_4. At the bottom of each compartment a platinum wire was sealed and was covered with finely powdered nickel oxide. The cell is provided with two sealed-on inlet tubes, one tube, f, which serves for hydroegn and the other, d, for the solution.

To introduce the nickel oxide into the vessel, the inlet side was cut off from the compartment part, a, at a point, marked c in the figure, as close as possible to the compartments, so that any nickel oxide which may adhere to the inner wall of the tube, c, may be reduced at the same temperature zone of the oven as is the oxide in the electrode compartments. After the introduction of nickel oxide the two parts were joined together and then the electrode vessel was connected with the other parts of the apparatus as shown in the figure.

The oven, T, was made of copper plate covered with thick asbestos plates and packed with asbestos fiber.

The hard glass flask H, of the capacity of 250 c.c. was the reservoir of a nickel sulphate solution and was fitted with a rubber stopper covered with bees-wax. Through this stopper was fitted a separating funnel K which served for conducting the solution into the flask and three tubes; one is an inlet of hydrogen, one which is connected to the trap J containing the same solution is an outlet of hydrogen, and the other one serves for introducing the solution into the electrode vessel. The other end of the tube L was thrust through the rubber stopper into one of the inlet tubes of the electrode vessel, d. Another flask, H′, of the same construction, served for the solution of the other concentration.

The hydrogen used was generated from Kipp's apparatus by the action of hydrochloric acid on Kahlbaum's C.P. zinc or pure electrolytic zinc and was purified by successively passing it through three alkaline solutions of potassium permanganate A_1, A_2, A_3, a layer of glass wool, B, and then over heated, fresh, palladized asbestos in the tube, C, to remove any trace of oxygen that might be present. Then the gas could be saturated with water vapour, before entering into the flask H, or H′ by passing humidifiers F_1 and F_2, or F_1' and F_2' with the same solution as is contained in the flask, Before the operation was started, all the parts of the apparatus were tested for its air-tightness.

In the reduction of nickel oxide, the hydrogen was introduced into the cell through the tube N, until all the air in the electrode vessel was washed out, with cocks i, k and then e, M being open.

The oven was put in its place and was gradually heated with three Bunsen burners. It was noticed that the reduction usually began at about 200°C., as was evidenced by the appearance of condensed water in the outlet tube of the gas. But the most part of the reduction was performed at 300°C. which is a temperature below the recognized transition point of nickel and the furnace was kept at this temperature for one hour more after the ceasing of water evolution, for the purpose of the assurance of complete reduction. During this operation the flow of hydrogen was kept at a rate of two or three bubbles per second. The condensed water was allowed to fall in the bent tube j, and to flow out from time to time through k by the pressure of hydrogen. Then the cell was left to cool to the room temperature, and was ready for being filled with the electrolyte, having been removed the furnace.

On the other hand, the electrolyte was freed from air in the following manner. Approximately the required amount of nickel sulphate solution was placed in the flask and purified hydrogen from the humidifiers was introduced into the flask. The gas bubbling up in small bubbles, saturating and stirring the whole liquid, left the flask through a trap. At the same time a part of the hydrogen was introduced into this reservoir also through the path N, e, L to replace the air in the tube L with hydrogen. After most of the air in the flask had been replaced by hydrogen, the stopcock G was closed and the flask was evacuated by an oil pump attached to the trap J. A mercury trap was also connected between the flask and the pump to prevent any back flow of air. G was then opened and the gas was readmitted slowly. This operation was repeated several times and the solution was made as free as possible from air and then the solution was preserved in the flask under an atmosphere of hydrogen to prevent the diffusion of oxygen from the atmosphere.

The electrolyte was allowed to flow down into the cell by the pressure of the gas. With the form of construction shown, it is an easy matter to fill the cell without leaving any bubbles of gas. The reservoir, l, of the cell was also filled with the same solution which served to rinse out the tube. The half-cell was then disconnected and placed in the thermostat where it was allowed to stand for half an hour before the electromotive force measurements were made. The filling up of the cell usually took about half an hour and therefore the first measurement was made one hour after the instant of the contact of the electrolyte with the nickel electrode. All the electromotive force measurements were made in a water thermostat, which was kept constant within 0.02°C.

For the measurements a Leeds and Northrup's K-type potentiometer and an H-type mirror galvanometer were used. As a standard of potential difference a Weston standard cell, which had been standardized by the Electrotechnical Laboratory of the Department of Communications, was used. A U-tube was used as the vessel for the junction solution. The decinormal calomel electrodes used were made from calomel prepared electrolytically and Kahlbaum's C.P. potassium chloride, and their potentials agreed very well with one another.

Results of Measurements of E.M.F. The combination of the cell was as follows:

Ni | $NiSO_4$ (0.05 or 0.005 M) | saturated KCl | KCl (0.1 N), Hg_2Cl_2 | Hg.

Table 2 contains the results of a series of measurements made on the cells of the solutions of the two different concentrations i.e. 0.05 M and 0.005 M. The time elapsed gives the hours after the contact of the electrolyte with the electrode.

TABLE 2.

E.M.F. of cell: Ni | $NiSO_4$ | sat. KCl | KCl(0.1N), Hg_2Cl_2 | Hg, at 25°C.

Elapsed time in hours	E.M.F. in volt.			
	0.05 M $NiSO_4$/L.		0.005 M $NiSO_4$/L.	
	Cell No. 1.	Cell No. 2.	Cell No. 3.	Cell No. 4.
1	−0.63860*	−0.63840	−0.66095*	−0.66032
2	−0.63860*	—	−0.66093*	−0.66030
3	—	—	—	−0.66255
4	−0.63858*	—	−0.66085*	—
12	−0.63846*	—	—	—
15	—	—	—	−0.6600
20	—	—	—	−0.6598
22	−0.63832**	—	−0.6604**	—
24	−0.63830**	—	—	—
36	−0.63810**	—	—	—
48	−0.63790**	—	−0.6600**	—
	H_2 on			
50	−0.63790	—	—	—
60	−0.63785	—	—	—

* After these measurements with cells Nos. 1 and 3 the temperature of the thermostat was lowered to 18°C. and measurements were made at this temperature, the results of which are given in Table 3.

** After the measurements at 18°C., the temperature was again raised to 25°C. and these measurements were made.

Each two of the platinum electrode wires of each cell were coated electrolytically with nickel from ammoniacal nickel sulphate solution, and covered with nickel powder in the manner already stated. The electrode thus prepared, having been annealed at about 300°C. gave the potential which agrees with that of the naked platinum, covered with nickel powder within about 0.05 millivolt.

The agreement of the potential of each two cells with the solution of the same concentration and constancy is very good as compared with the results of the previous investigators. The change in potential of the same cell was not greater than 0.5 millivolt for 24 hours. Furthermore, the electromotive force was reversible with respect to temperature as will be shown in the next paragraph. Besides, it was observed that the electromotive force changed by not more than 0.05 millivolt by the passage of hydrogen through the solution in the cell for about half an hour which was done at the end of the measurements with cell No. 1 and also that by shaking the powdered electrode, the values of the electromotive forces fluctuated around a certain corresponding value temporarily, but did not show any tendency to change continuously in one direction.

The measurements of the electromotive force were made also at 18°C. with cells Nos. 1 and 3, after twelve hours measurement at 25°C. in the case of the former cell and after four hours measurement in the case of the latter. The results at 18°C. are given in Table 3.

After the measurements at 18°C., the temperature was again raised to 25°C. and further measurements were made, the results of which are given in Table 2. It will be observed that there is no hysteresis but only a continuous and slow lowering of the electromotive force.

TABLE 3.

E.M.F. of cell : Ni | $NiSO_4$ | sat. KCl | KCl(0.1 N), Hg_2Cl_2 | Hg, at 18°C.

	Mols $NiSO_4$ per litre	E.M.F. in volt.
Cell No. 1	0.05	−0.63820
Cell No. 3	0.005	−0.66105

By the combinations of data for cells No. 1 and No. 3, given in Table 2 and Table 3, it will be found that the difference in electromotive force between 18°C. and 25°C. are 0.00066 and 0.00020 volt for the cells of 0.05 and 0.005 mol, respectively. Taking the difference in the potential of the standard decinormal calomel electrode between these two temperatures as

-0.00040 volt[1], the temperature coefficients of these cells are calculated to be:

$$\frac{dE}{dt} = -0.00009 \text{ volt per degree for the 0.05 mol } NiSO_4.$$

$$\text{"} = -0.00003 \text{ " " " " " " 0.005 " " .}$$

Calculation of Normal Electrode Potential. The normal electrode potential was computed on the ground of two different concepts of the strong electrolytes, one being that the ion concentration is involved in the expression of the electromotive force of the concentration cell and the other being that the activity of the ion is involved.

(1) *Ion concentration being used.* The normal electrode potential E_0 can be calculated by using the following well-known eqution

$$E = E_0 + \frac{RT}{2F} \ln Ca \qquad (1)$$

where E is the potential in the solution used, referred to the molal hydrogen electrode, C is the concentration of the solution in mols per litre and a is its degree of ionization which is defined by $\frac{\lambda}{\lambda_0}$ for a dilute solution or by $\frac{\lambda\eta}{\lambda_0\eta_0}$ for a concentrated solution. As the values of λ, and ionic conductance of nickel ion, from which λ_0 must be calculated, given in Kohlrausch-Holborn's table of conductances are inaccurate and the viscosity data are lacking, the writer's own values were used[2].

The data in Table 2 give, as a mean value for the cell,

$Ni \mid NiSO_4(0.05\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $e = -0.6385$ volt at 25°C.

Taking the potential of the decinormal calomel electrode, Ec, to be -0.3376 volt, $H_2 \mid H^+(1\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $Ec = -0.3376$ volt,

then $Ni \mid NiSO_4(0.05\ M) \parallel H^+(1\ M) \mid H_2$; $E = -0.3009$ volt.

For 0.05 M nickel sulphate solution, the values of λ, λ_0 and $\frac{\eta}{\eta_0}$ at 25°C. are 50.75, 133.0 and 1.0175, respectively and

$$a = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3883$$

Then, we obtain $-0.3009 = E_0 + 0.02958 \log 0.05 \times 0.3883$

from which $E_0 = -0.2503$ volt at 25°C.

Similarly, as the mean value for the cell,

$Ni \mid NiSO_4(0.005\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $e = -0.6607$ volt at 25°C.

and $H_2 \mid H^+(1\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $Ec = -0.3376$ volt at 25°C.

Combining these two, we obtain

$Ni \mid NiSO_4(0.005\ M) \parallel H^+(1\ M) \mid H_2$; $E = -0.3231$ volt at 25°C.

(1) Clark, "Determination of hydrogen ions," (1920), p. 203.

(2) This journal, **3** (1928), 47.

Taking $\frac{\lambda}{\lambda_0}=82.69/133=0.62173$ as the degree of ionization of 0.005 M $NiSO_4$. By equation (1), we obtain

$$-0.3231=E_0+0.02958 \log 0.005\times 0.62173$$

from which $E_0=-0.2489$ volt at 25°C.

Consequently, as a mean value of the potential for the electrode $Ni \mid Ni^{++}(1M)$, we find $E_0=-0.2496\pm 0.0007$ volt at 25°C.

In a similar manner, E_0 at 18°C. was calculated. The electromotive force of the cell,

$Ni \mid NiSO_4(0.05\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg$; $e=-0.6382$ volt at 18°C.

Taking the potential of the decinormal calomel electrode to be -0.3380 volt, then, $Ni \mid NiSO_4(0.05\ M) \parallel H^+(1\ M) \mid H_2$; $E=-0.3002$ volt.

For 0.05 M $NiSO_4$, the values of λ, λ_0 and $\frac{\eta}{\eta_0}$ at 18°C. are 43.833, 113.6 and 1.0209, respectively and

$$a=\frac{\lambda\eta}{\lambda_0\eta_0}=\frac{43.833\times 1.0209}{113.6}=0.3939.$$

Inserting these values in equation (1), we obtain

$$-0.3002=E_0+0.02888 \log 0.05\times 0.3939$$

$$E_0=-0.2509 \text{ volt at } 18°C.$$

The electromotive force for the cell,

$Ni \mid NiSO_4(0.005\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg$; $e=-0.66105$ volt at 18°C.

Subtracting the potential of the decinormal calomel electrode from this value, we obtain $Ni \mid NiSO_4(0.005\ M) \parallel H^+(1\ M) \mid H_2$; $E=-0.32305$ volt.

And, $$a=\frac{\lambda}{\lambda_0}=\frac{70.89}{113.6}=0.62403.$$

Then, $E_0=-0.2507$ volt at 18°C.

We find, as a mean value,

$$E_0=-0.2508\pm 0.0001 \text{ volt at } 18°C.$$

(2) *Activity of the ion being used.* If the activity of the ion, but not the ion concentration, is considered to be involved in the free energy change in the cell, the normal electrode potential E_0 at the unit activity of the ion must be calculated by the equation

$$E=E_0+\frac{RT}{2F}\ln m\,\gamma_{Ni^{++}} \qquad (2)$$

where $\gamma_{Ni^{++}}$ is the activity coefficient of the nickel ion at the molarity m of nickel sulphate.

Unfortunately, there are no data from which the activity coefficients of the nickel ion can be calculated. But, Lewis and Randall[1] have compiled a

(1) Lewis and Randall, "Thermodynamics," (1923), p. 382.

table of the activity coefficients of individual ions at various ionic strengths by using certain assumptions. This table shows that the activity coefficients of ions of the same valency are nearly the same when the ionic strengths are not large. Therefore, without any other means for the time being until the actual measurements of the activity of the nickel ion can be made, an attempt was made to calculate the normal potential of nickel on the assumption that the activity coefficients of the nickel ion are the same as those of bivalent ions given in the table above cited. The necessary values at the ionic strengths used in this investigation were obtained by an interpolation or an extrapolation.

The electromotive force of the cell,

$Ni \mid NiSO_4(0.05\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg$; $e = -0.6385$ volt at 25°C.

Taking Lewis and Randall's value of the potential of the decinormal calomel electrode[1].

$H_2 \mid H^+(1\ M \text{ of } a_{H^+}) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg$; $Ec = -0.3351$ volt at 25°C.

By the combination of these two,

$Ni \mid NiSO_4(0.05\ M) \parallel H^+(1\ M \text{ of } a_{H^+}) \mid H_2$; $E = -0.3034$ volt at 25°C.

By a slight extrapolation from the table of activity coefficients of individual ions, we find the activity coefficient of bivalent metallic ion to be 0.24 at this concentration. Taking the activity coefficient of nickel ion for 0.05 M $NiSO_4$ as 0.24, we obtain for the above cell

$$-0.3034 = E_0 + 0.02958 \log 0.05 \times 0.24,$$

from which $E_0 = -0.2466$ volt at 25°C.

The electrolotive force of the cell

$Ni \mid NiSO_4(0.005\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg$; $e = -0.6607$ volt at 25°C.

from which

$Ni \mid NiSO_4(0.005\ M) \parallel H^+(1\ M \text{ of } a_{H^+}) \mid H_2$; $E = -0.3256$ volt at 25°C.

The value of $\gamma_{Ni^{++}}$ at 0.005 M is 0.53. Substituting these values in equation (2),

$$-0.3256 = E_0 + 0.02958 \log 0.005 \times 0.53,$$

we obtain $E_0 = -0.2494$ volt at 25°C.

As a mean value, $E_0 = -0.2480 \pm 0.0014$ volt at 25°C.

Similarly, we may calculate E_0 at 18°C. For this purpose, however, it is necessary to evaluate the potential at 18°C. of decinormal calomel electrode referred to the standard hydrogen electrode.

The electromotive force measurements of the cell, $H_2 \mid HCl(0.1\ M),\ Hg_2Cl_2 \mid Hg$, by J. H. Ellis[2] give -0.3978 volt at 18°C. Using this observed value, and taking 0.814 as the activity coefficient of 0.1 molal acid,

(1) Lewis and Randall, "Thermodynamics," (1923), p. 406.

(2) Ellis, *J. Am. Chem. Soc.*, **38** (1916), 754.

the electromotive force of the cell where both a_{H^+} and a_{Cl^-} are equal to unity can be calculated by the following equation.

$$-0.3978 = E_0 + \frac{RT}{F} \ln a_{H^+} a_{Cl^-} = E_0 + \frac{2RT}{F} \ln m a_{\pm}$$

$E_0 = -0.3978 - 0.1853 \log 0.1 \times 0.814 = -0.2720$ volt at 18°C. see Vol. 3, p. 321

From this value, the potential of the decinormal calomel electrode at 18°C. can be calculated by the equation

$$H_2 | H^+(1\ M \text{ of } a_{H^+}) \| KCl(0.1\ N), Hg_2Cl_2 | Hg; \quad E = E_0 - \frac{RT}{F} \ln \frac{1}{a_{Cl^-}}$$

Taking 0.794 as the activity coefficient of 0.1 molal KCl[1] and accordingly as that of chloride ion in the same solution, we obtain $E = -0.3355$ volt at 18°C. Combining this value with the results given in Table 3, E_0 of the nickel electrode at 18°C. can be calculated.

Let us first consider the cell

$Ni | NiSO_4(0.05\ M) \| KCl(0.1\ N), Hg_2Cl_2 | Hg$; $e = -0.6382$ volt at 18°C.,

then, $Ni | NiSO_4(0.05\ M) \| H^+(1\ M \text{ of } a_{H^+}) | H_2$; $E = -0.3027$ volt at 18°C.

By equation (2), $-0.3027 = E_0 + 0.02888 \log 0.05 \times 0.24$

$E_0 = -0.2472$ volt at 18°C.

Similarly, for the cell

$Ni | NiSO_4(0.005\ M) \| KCl(0.1\ N), Hg_2Cl_2 | Hg$; $e = -0.66105$ volt at 18°C.

$Ni | NiSO_4(0.005\ M) \| H^+(1\ M \text{ of } a_{H^+}) | H_2$; $E = -0.32555$ volt at 18°C.

$-0.32555 = E_0 + 0.02888 \log 0.005 \times 0.53$

$E_0 = -0.2511$ volt at 18°C.

Consequently, as a mean value

$E_0 = -0.2492 \pm 0.002$ volt at 18°C.

For comparison, the values of normal electrode potentials calculated in the above are summarised in Table 4.

TABLE 4.

Values of normal electrode potential in volt.

	(1) Calculated from ion concentration.		(2) Calculated from ion activity.	
	25°C.	18°C.	25°C.	18°C.
From 0.05 M $NiSO_4$	−0.2503	−0.2509	−0.2466	−0.2472
From 0.005 M $NiSO_4$	−0.2489	−0.2507	−0.2494	−0.2511
Mean	−0.2496±0.0007	−0.2508±0.0001	−0.2480±0.0014	−0.2492±0.002

It is important to have found out that, although the nickel electrodes are those which were prepared by reducing finely divided nickel oxide in an

(1) Lewis and Randall, "Thermodynamics," (1923), p. 362.

atmosphere of hydrogen, and probably some hydrogen was occluded in them, these values of E_0 calculated from the measurements with different concentrations are in perfect agreement with each other at the same temperature.

On the other hand, those values which were calculated from the activities of the ion of the two different concentrations are not so excellent agreement at both 18°C. and 25°C. as in the case of the values from the ion concentrations, though the difference amounts to only a few millivolts. This lack of agreement is probably due to the assumption involved in the calculation of activity of nickel ion. It is expected that more concordant results will be obtained if the activity of the nickel ion is measured accurately.

Change in Free Energy of Nickel Electrode Reaction. The change in free energy of the formation of nickel from its ion per equivalent, that is, $\frac{1}{2}Ni^{++}+\ominus=\frac{1}{2}Ni$, is expressed by the thermodynamic equation,

$$-\Delta F = E_0 F.$$

Taking as the values of E_0 at 25°C. -0.2496 volt which is the average of the normal electrode potential of nickel at one mol of ion concentration, we obtain, $\Delta F = 0.2496 \times 96500/4.182 = 5759$ calories at 25°C.

In a similar way, taking -0.2508 volt as the mean value of E_0 at 18°C., we obtain, $\Delta F = 5787$ calories at 18°C.

On the other hand, if we take the value of E_0 as -0.248 volt at 25°C. which is the average of the potentials at unit activity, then

$\Delta F = 5723$ calories at 25°C.

Similarly, from the value of -0.2492 volt at 18°C.

$\Delta F = 5750$ calories at 18°C.

These investigations were carried on under the direction of Professor G. Fuseya, with the aid of a grant made to him by the Saito Gratitude Foundation in Sendai, the writer wishes to express his great indebtedness, to him. The writer wishes to express his thanks also to Professor M. Katayama (Tokyo) for his counsel in several matters.

Summary.

1. A reproducible electrode, which gives a constant and reversible potential of active nickel was obtained by using powdered nickel reduced with hydrogen directly in the cell and also using an apparatus which allows the cell to be filled with the electrolyte entirely in the absence of air.

2. The potentials of the reduced nickel powder in 0.05 M and 0.005 M nickel sulphate solutions both at 25°C. and 18°C. were measured in an atmosphere of hydrogen.

3. The normal electrode potentials of nickel were calculated from these observed potentials on the ground of two different concepts of the strong electrolytes, one being that the ion concentrations calculated from the conductance viscosity ratios are involved in the expression of the electromotive force of a concentration cell and the other being that the ion activities are involved. The average values of these normal electrode potentials are -0.2496 volt (25°C.) and -0.2508 volt (18°C.) at one molal ion concentration, and -0.2480 volt (25°C.) and -0.2492 volt (18°C.) at one molal ion activity.

4. The change in free energy of nickel electrode reaction per equivalent, that is, $\frac{1}{2}Ni^{++}+\ominus=\frac{1}{2}Ni$ was calculated from the above electrode potentials.

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ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN(1). I. THE AKITA HOKUTOLITE.

By Ichizo SUGANUMA.

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The Constituents and Genesis of the Akita Hokutolite Produced from a Sulphurous Hot Spring called Shikayu in Akita Prefecture. A heavy crystalline mineral produced from a sulphurous spring in Akita-ken, a province of Japan, is very similar in its appearance and properties to hokutolite from the Hokuto Spring in Taiwan i. e. Formosa.(2) Some mineralogists of this country supposed that the former mineral is of the same kind as the latter, but this not being proved by any accurate experiments, the author analysed and examined the former mineral, and has obtained the result that it is of the same kind as hokutolite. Therefore the author thinks that the mineral can properly be called the *Akita hokutolite.* The chief constituents of the Akita hokutolite are $BaSO_4$ and $PbSO_4$, and the mineral consists of the isomorphous mixture of the above constituents just as the Taiwan hokutolite does, but the former differs from the latter in the following points:—

(1) The different samples of the Akita hokutolite vary in a wide range in their compositions i. e. the ratios of $BaSO_4$ and $PbSO_4$ contained in them,

(1) Read before the Chemical Society of Japan, July 11, 1922.

(2) Okamoto, *J. Geol. Soc. Tokyo,* 18 (1911), 19; *Beitr. Mineral. Japan,* 4 (1912), 178; Hayakawa and Nakano, *Z. anorg. Chem.*, 78 (1912), 183; Richards and Sameshima, *J. Am. Chem. Soc.*, 42 (1920), 928.

while the composition of the Taiwan hokutolite is approximately constant.

(2) Generally, $BaSO_4$ predominates in the former mineral than in the latter, and sometimes is nearly equal to a mineral barite.

(3) The Taiwan hokutolite is always of brown colour, while the Akita hokutolite is sometimes of light yellow or even white, besides the ordinary kind of brown colour.

(4) As a remarkable difference, the accompanying rare elements of the Akita hokutolite are much greater in kinds than those reported on the Taiwan hokutolite, especially, the radioactivity of the mineral is not only ascrived to the radio-active elements of radium series but to the radio-active elements of thorium series, because the presence of thorium and its active deposits has been proved by the chemical analysis and the radioactive experiments.

(5) The commonest kind of the Akita hokutolite is composed from a great number of small rhombic brownish crystals as the Taiwan hokutolite, but the former contains thin white layers in regular intervals i. e. a zonal structure of the two layers of brown and white, while such two different layers are not clearly perceived in the latter mineral.

The author separated the two layers of the Akita hokutolite from each other and analysed each layer in order to find out the difference between the compositions of the two layers.

The results of the analysis show that in the white layer $BaSO_4$ is much greater than in the brownish layer, and also SiO_2 is somewhat greater, while in the brownish layer predominate PbO and FeO as $PbSO_4$ and probably PbS_5O_6, x FeS_5O_6. The author ascrives the brownish colour of the mineral to pentathionate of Pb and Fe from several experimental facts.

The ordinary metallic elements contained as impurities in the Akita hokutolite are Sr, Ca, Mg of Ba group with Al and Fe ; and further the presence of the rare metallic elements such as Ti, Zr, Th, Ce, La, Pd and Nd, and Ra, Rn, Po of U series has been determined qualitatively (but some quantitatively) in the mineral.

Among these, the presence of Th has been ascertained by the analytical results and by tracing the decay curve of active deposits of Th emanation, but radium accompanying Ba salts in a very minute quantity is proved only by the radio activity of the solid salts and by determining half period of radium emanation evolved from the solution of those salts.

As to uranium, the mother element of radium, the author could only find a trace of it by the colour reaction with $K_4Fe(CN)_6$, but polonium, one of the transformation products of radium, could easily be detected by its characteristic chemical reactions and by plotting the decay curve particular to the metallic film of Po deposition on the bismuth plate.

Therefore, the radio activity of the Akita hokutolite is due to the several radio active elements belonging to radium series and thorium series.

In regard to the genesis of the Akita hokutolite, the author has found the facts that it is deposited only on the rock surface which is covered or washed by the spring water cooled to the temperature of 40°C. and that this temperature highly favours the growth of Cyanophyceae, and further that the gelatinous matter contained in these Cyanophyceae causes the coagulation of silicic acid hydrosol from the acidic solution containing aluminium ion just as the ordinary gelatine or albumen does.

Thus the author has come to assume that the components of the hokutolite come gradually to coat the rock surface by the aid of the silicic acid hydrogel.

In regard to the zonal structure of the hokutolite i. e. white and brown layers, the author considers that the white layer, which is mostly composed of matters with very insoluble properties such as $BaSO_4$, is formed by a current of the strongest acidity and also of the highest temperature.

Such an acidity and temperature can exist only with the smallest supply of the river water in the coldest season.

Pentathionate and sulphide of lead and iron are almost dissolved by such a hot acidic current. Thus we have a white layer and a white deposition. Sometimes in this season, the upper dried part of the rock above the surface of the current, exposes Cyanophyceae to the coldest atmospheric air and destroys the vegetable constitutions, leaving behind a gelatinous or slimy matter. The rock surface naturally absorbs the splashes of the river water and coagulates silicic acid hydrosol contained in them.

This conclusion on the formation of the white layer in the coldest season is pretty well confirmed by the surfaces of those samples which the author collected in that season.

In regard to the brown layer of the hokutolite, the gelatinous matter produced by the natural metabolysm of Cyanophyceae first coagulates silicic hydrosol and gradually adsorbs more and more of those brown components insoluble in the warm dilute acid.

Besides, the author observes about some other specimens that Cyanophyceae are totally destroyed by the cold flood of melted snow in the spring season. In most of these cases, the gelatinous matter contained, cooperates with the aluminium ion in the river current in coagulating the silicic hydrosol forming a muddy brown deposition. In either of these cases, the brown layer contains a comparatively larger proportion of lead and iron compounds soluble in acid water at a higher temperature than 40°C.

In fact the sample of the Akita hokutolite collected in the lowest part of the current contains the largest proportion of lead, but that collected in the vicinity of the source of the spring the smallest proportion of lead and iron as shown by the Table 2.

The latter sample, which is very near to barite in its composition, appears to have been deposited upon rocks exposed out of the river surface, the hot water splashing out energetically from a certain spring, having been cooled down. It is probable that these depositions have been cemented by the colloidal silicic acid precipitated first, because when the hot water of the spring source is collected in a beaker and allowed to cool for a while, the clear liquid gradually becomes cloudy and precipitates colloidal silicic acid hydrogel as has been observed by the author.

The following tables show the compositions of the white and brown layers in the Akita hokutolite compared (Table 1), and the compositions of the samples collected in the vicinity of the spring source and at the lowest part of the river current (Table 2), as well as the composition of the spring source itself (Table 3).

TABLE 1.

Compositions of the white and brown layers of the Akita hokutolite:

Component	White layer	Brown layer	Component	White layer	Brown layer
PbO	6.45	9.72	K_2O	0	0
BaO	55.33	53.80	Na_2O	—	—
SrO	0.11	0.08	SiO_2	4.61	2.53
CaO	0.34	0.32	SO_3	31.43	32.19
MgO	0.25	0.25	As_2O_5	(0.01)	—
Fe_2O_3(CeO_2, ThO_2, etc.)	0.43	0.54	NH_4Cl	—	(0.02)
Al_2O_3	0.52	0.47	total	99.48 %	99.92 %

TABLE 2.

Compositions of the samples collected in the vicinity of the spring source and at the lowest part of the hot river current:

Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.	Component	Sample at the upper part of the spring.	Sample at the lowest part of the river.
BaO	62.18	48.47	MgO	—	0.20
PbO	4.61	15.04	SiO_2	0.44	3.28
Fe_2O_3 }	0.26	0.52	SO_3	32.49	30.31
Al_2O_3 }					
CaO	—	0.38	total	99.98 %	98.20 %

TABLE 3.

Composition of the spring source called Akita Shikayu.
(1000 parts taken ; temperature of the spring 97°C., strong acid.)

$BaSO_4$	0.0011	$NaCl$	0.1121
$PbSO_4$	0.0009	NH_4Cl	0.0003
$FeSO_4$	0.1832	HCl	2.5497
$Al_2(SO_4)_3$	0.8610	H_2SO_4	0.4247
$CaCl_2$	0.0033	H_2SiO_3	0.3436
$MgCl_2$	0.0581	H_3BO_3	tr.
$AsCl_3$	0.0027	$ZrCl_4$	tr.
KCl	0.0752		

The First Higher School, Tokyo.

ON THE CONSTITUENTS AND GENESIS OF A FEW MINERALS PRODUCED FROM HOT SPRINGS AND THEIR VICINITIES IN JAPAN. II. COMPOSITION AND GENESIS OF SOLUBLE SULPHATES PRODUCED IN THE ENVIRONMENTS OF A SULPHUROUS SPRING.

By Ichizo SUGANUMA.

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The so-called sulphurous gas gushing out from the cavities which are located in a region of sulphurous spring, chiefly consists of H_2S, CO_2, and steam or vapour. If the gas contains steam or vapour in a large amount, the temperature of the gas mostly attains about 100 degrees.

The sulphurous gas above explained, gushing from the fissure of the andesite rock or the cavity of clay which is formed by the decomposition of the andesite, gradually acts physically and chemically on the surface of the rock or clay above mentioned.

As the result of these action, a long needle-like crystalline efflorescence of white or light yellow with a silky appearance, is deposited on the surface.

An alum spring in the vicinity of Beppu in Oita-ken, a province of Kyushu, Japan, gives us a large amount of these crystalline masses by the natural production above mentioned, and in Nasu-Motoyu in the vicinity of Nikko, and also in Owaku-dani in Hakone. These natural crystalline products are collected and utilized for both bathing and medical purposes.

These crystals under microscope have a fibrous structure mostly with a few opaque nodes as on grasses, generally white in colour, but sometimes of light yellowish white, or yellow, or even mixed with yellowish powder of native sulphur.

The needle-like, silky white crystals, which are of the commonest kind, have a melting point 105°C., are soluble in water, and the aqueous solution of them is strongly acid.

The composition of the crystals is $Al_2(SO_4)_3$ and $FeSO_4$, and contains the same molecules of water of crystallization as in the common alum. In mineralogy, these crystals are called *halotrichite*.

The author obtained these crystals experimentally by passing steam mixed with H_2S and CO_2 on the Hakone andesite finely powdered and well washed, and on another experiment obtained the same result by passing steam through the andesite powder which was percolated with a dilute H_2SO_4, and allowing it to stand on a glass plate for a few days.

Therefore we know that the genesis of the crystals above mentioned is due to the weathering action of aluminium silicate and iron silicate contained in the andesite by carbonic acid or the other acids, and at the same time, to the formation of aluminium sulphate and iron sulphate by the action of H_2SO_4 produced by the oxidation of H_2S.

In the same region of sulphurous spring that produces halotrichite, there are found other snow-white crystalline masses similar in appearance to the above mineral.

These crystals under a microscope are found to be transparent, colourless and scaly, and they have a melting point 115°C.

The composition obtained by chemical analysis corresponds to $Al_2(SO_4)_3 \cdot 16H_2O$ i.e. a mineral called *alunogen* mineralogically. The author observed certain samples which consist of halotrichite on the top and of alunogen on the base, and sometimes observed the facts that alunogen is chiefly formed on clay longly exposed to air and sulphurous gas and fully decomposed by acids.

On these facts it is supposed that alunogen is formed from the clay poor in iron, subjected under the action of sulphurous gas, while the clay at first rich in iron, produces halotrichite.

Furthermore, the author observed the existence of light green crystalline masses as efflorescence on a black volcanic rock in Taiwan or some dark green clay in Fukeno-yu, Akita prefecture. The formation of these crystals is probably due to the action of sulphurous gas on rocks or clay very rich in iron, and the composition and properties of the crystals correspond to $FeSO_4 \cdot 7H_2O$ i.e. native green vitriol or *melanterite* in mineralogy. The fact that the samples of these crystals are frequently contaminated with halo-

trichite when tested under a microscope, is easily accounted for by the above reasoning of their formation.

Now, rocks with melanterite and halotrichite formed on their surfaces, are found to contain some fine crystalline particles of FeS_2 i. e. iron pyrites in their small cavities. Probably this is the case of the formation of FeS_2 by the interaction of hydrogen sulphide and iron silicate in the absence of air.

The author has frequently observed the fact that gypsum exists on a rock surface where the steam in sulphurous gas is gradually condensed. This mineral is, no doubt, formed from calcium silicate contained in rocks by the action of H_2SO_4, which is an oxidized product of H_2S.

It is a noticeable fact that a sulphurous gas containing only a small proportion of water vapour and naturally dry gas mixture composed of H_2S and CO_2 of ordinary temperature, frequently acts as a very poisonous gas as war gas. Some examples of this are found in the sulphurous gas in Sessho-seki in Nasu, and Sessho-dani in Akita Shika-yu, Akita Prefecture, Japan.

TABLE 1.

Analytical results of alunogen.

Component	Observed value	Calc. value as $Al_2(SO_4)_3 \cdot 16H_2O$
Al_2O_3	16.17	16.22
FeO	tr.	—
MgO	tr.	—
CaO	0.30	—
SO_3	38.01	38.09
H_2O	45.13 (at 325°C.)	45.69
SiO_2 (in sol. in acids)	0.23	—
total	99.84	100.00

TABLE 2.

Analytical results of halotrichite.

Component	Observed value	Calc. value as $Al_2(SO_4)_3 \cdot FeSO_4 \cdot 24H_2O$
Al_2O_3	10.28	11.03
FeO	8.56	7.75
MgO	0.12	—
CaO	0.46	—
SO_3	34.85	34.56
H_2O	44.82 (at 325°C.)	46.66
SiO_2 (insol. in acids)	1.24	—
total	100.33	100.00

TABLE 3.

Analytical results of melanterite.

Component	Observed value	Calc. value as $FeSO_4 \cdot 7H_2O$
FeO	25.25	25.90
Al_2O_3	2.12	—
CaO	0.46	—
MgO	0.36	—
SO_3	27.65	28.77
H_2O	—	45.33
total	—	100.00

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ON THE OXIDATION OF SODIUM SULPHITE IN SODIUM CARBONATE SOLUTION WITH AIR.

By **Susumu MIYAMOTO.**

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In connection with the former study on the effect of sodium hydroxide on the oxidation of sodium sulphite[1] with air, the present research was carried out under the same condition, expecting that it will be able to calculate the dissolution velocity of oxygen into sodium carbonate solution from the result.

The experimental procedure was quite the same as that described in the previous paper[2]. In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of sodium sulphite; k was calculated by $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$; $v_{calc.}$ was obtained by $v_{calc.}=v_0-kt$, using the mean value of k. The value of k, when $C_{Na_2CO_3}=0$, given in the following tables, is that obtained in the previous study[3].

(1) S. Miyamoto, this journal, **2** (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40.

(2) Ibid.

(3) Ibid.

Table 1.

Temp. = 20°C. Velocity of air = 7.78 litres per hour.

$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0	—	—	—	0.330
0.01875	0	23.57	—	—
	10	20.81	20.72	0.276
	25	16.43	16.44	0.286
	50	9.14	9.32	0.289
	0	19.24	—	—
	10	16.48	16.39	0.276
	20	13.22	13.54	0.301
	40	6.99	7.84	0.306
	0	14.62	—	—
	10	11.84	11.77	0.278
	20	9.13	8.92	0.275
	35	4.50	4.64	0.289
	0	11.31	—	—
	9	8.78	8.74	0.281
	15	7.04	7.03	0.285
	25	4.45	4.18	0.274
			Mean:	0.285
0.0375	0	22.53	—	—
	10	19.82	19.89	0.271
	20	17.13	17.25	0.270
	50	9.12	9.33	0.268
	0	20.81	—	—
	10	18.16	18.17	0.265
	20	15.81	15.53	0.250
	50	7.20	7.61	0.272
	0	16.15	—	—
	10	13.48	13.51	0.267
	20	10.94	10.87	0.261
	45	4.80	4.27	0.252
			Mean:	0.264
0.0750	0	18.91	—	—
	10	16.34	16.42	0.257
	25	12.42	12.68	0.260
	50	6.36	6.46	0.251
0.0750	0	18.08	—	—
	10	15.61	15.59	0.247
	25	12.01	11.85	0.243
	50	6.05	5.63	0.241
	0	11.58	—	—
	9	9.39	9.34	0.243
	20	6.58	6.60	0.250
			Mean:	0.249
0.1875	0	22.77	—	—
	10	20.32	20.39	0.245
	25	16.61	16.82	0.246
	55	9.47	9.68	0.242
	0	15.14	—	—
	10	12.74	12.76	0.240
	25	9.14	9.19	0.240
	50	4.33	3.24	0.216
	0	12.44	—	—
	9	10.26	10.30	0.242
	20	7.49	7.68	0.248
	35	4.50	4.11	0.227
			Mean:	0.238
0.2625	0	20.21	—	—
	10	17.82	17.94	0.239
	25	14.40	14.53	0.232
	55	7.50	7.72	0.231
	0	14.32	—	—
	10	11.97	12.05	0.235
	25	8.64	8.64	0.227
	0	13.49	—	—
	10	11.21	11.22	0.228
	25	7.96	7.81	0.221
	45	4.29	3.27	0.204
			Mean:	0.227
0.3750	0	19.18	—	—
	10	16.95	16.97	0.223
	25	13.75	13.65	0.217
	55	7.20	7.58	0.218

TABLE 1. (Continued.)

Temp.=20°C. Velocity of air=7.78 litres per hour.

$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.3750	0	19.00	—	—
	10	16.72	16.79	0.228
	25	13.31	13.47	0.228
	0	14.53	—	—
	10	12.33	12.32	0.220
	25	8,94	9.00	0.224
	45	5.22	4.58	0.207
			Mean:	0.221
0.563	0	22.20	—	—
	15	19.41	19.38	0.186
	30	16.76	16.56	0.181
	0	21.82	—	—
	10	19.84	19.94	0.198
	25	16.92	17.12	0.196
	55	11.40	11.48	0.189
	0	14.47	—	—
	15	11.74	11.65	0.182
	30	8.82	8.83	0.188
	55	4.58	4.13	0.180
			Mean:	0.188
0.750	0	24.77	—	—
	10	23.06	23.12	0.171
	30	19.60	19.82	0.172
	60	14.37	14.87	0.173
	0	23.93	—	—
	10	22.30	22.28	0.163
	25	19.79	19.80	0.166
	60	14.33	14.03	0.160
	0	14.75	—	—
	15	12.29	12.27	0.164
	30	9.79	9.80	0.165
	60	5.57	4.85	0.153
			Mean:	0.165
0.938	0	25.63	—	—
	15	23.30	23.38	0.155
	30	21.18	21.13	0.148
	60	16.63	16.63	0.150
0.938	0	19.61	—	—
	15	17.39	17.36	0.148
	30	15.11	15.11	0.150
	60	10.36	10.61	0.154
	0	14.39	—	—
	15	12.22	12.14	0.145
	30	10.09	9.89	0.143
	60	5.05	5.39	0.156
			Mean:	0.150
1.125	0	23.95	—	—
	10	22.58	22.62	0.137
	25	20.61	20.62	0.134
	50	17.25	17.30	0.134
	0	22.88	—	—
	15	20.89	20.88	0.133
	30	18.92	18.89	0.132
	60	14.57	14.90	0.139
	0	14.17	—	—
	15	12.37	12.17	0.120
	30	10.24	10.18	0.131
	60	5.97	6.19	0.137
			Mean:	0.133
1.313	0	28.49	—	—
	25	25.29	25.41	0.128
	50	22.49	22.34	0.120
	0	25.08	—	—
	25	21.80	22.00	0.131
	50	18.97	18.93	0.122
	0	14.99	—	—
	15	13.27	13.14	0.115
	30	11.45	11.30	0.118
	55	8.47	8.22	0.119
	0	12.34	—	—
	15	10.31	10.49	0.135
	30	7.74	8.65	0.120
	55	5.83	5.57	0.118
			Mean:	0.123

The Effect of Sodium Carbonate. Table 1 shows that the oxidation velocity of sodium sulphite in sodium carbonate solution decreases with the increase of the concentration of the latter, quite the same way as in the case of its oxidation in sodium hydroxide solution. The velocity constant seems to be expressed as a linear function of $C_{Na_2CO_3}$, when $C_{Na_2CO_3}$ is greater than about 0.02 normal; $k_{calc.}$ in Table 3 was calculated by $k_{calc.}=0.258-0.114\ C_{Na_2CO_3}$.

TABLE 2.

Velocity of air = 7.78 litres per hour.

Temp.	$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	0.1875	0	22.28	—	—
		10	19.48	19.57	0.280
		25	15.25	15.50	0.281
		55	7.42	7.37	0.270
		0	15.52	—	—
		10	12.96	12.81	0.256
		20	10.18	10.10	0.267
		40	4.62	4.68	0.273
				Mean:	0.271
30°C.	0.3750	0	24.77	—	—
		10	22.26	22.28	0.251
		30	17.47	17.30	0.243
		60	9.85	9.83	0.249
		0	15.78	—	—
		10	13.28	13.29	0.250
		20	10.76	10.80	0.251
		45	4.67	4.57	0.247
				Mean:	0.249
30°C.	0.938	0	29.33	—	—
		10	27.53	27.62	0.180
		30	23.89	24.20	0.181
		60	18.95	19.07	0.173
		0	14.51	—	—
		15	12.10	11.94	0.161
		30	9.47	9.38	0.168
		60	4.13	4.25	0.173
		0	12.17	—	—
		15	9.73	9.60	0.163
		30	7.23	7.04	0.165
		55	2.77	2.76	0.171
				Mean:	0.171

TABLE 2. (Continued.)

Velocity of air = 7.78 litres per hour.

Temp.	$C_{Na_2CO_3}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
40°C.	0.1875	0	23.96	—	—
		10	21.06	21.08	0.290
		25	16.51	16.76	0.298
		55	8.29	8.12	0.285
		0	15.33	—	—
		10	12.44	12.45	0.289
		20	9.61	9.57	0.286
		40	4.05	3.81	0.282
				Mean:	0.288
40°C.	0.3750	0	22.82	—	—
		15	18.68	18.93	0.276
		30	15.03	15.05	0.260
		60	7.53	7.28	0.255
		0	15.94	—	—
		10	13.33	12.35	0.261
		20	10.91	10.76	0.252
		45	4.69	4.28	0.250
				Mean:	0.259
40°C.	0.938	0	23.67	—	—
		15	20.97	20.82	0.180
		30	17.68	17.97	0.200
		60	11.96	12.27	0.195
		0	14.15	—	—
		15	11.17	11.30	0.199
		30	8.75	8.45	0.180
		55	3.90	3.70	0.186
				Mean:	0.190

The Effect of Temperature. The results of the measurements at 30°C. and 40°C. are given in Table 2. The effect of temperature was small, as can be expected.

$$\frac{k_{30°}}{k_{20°}} = \frac{0.271}{0.238} = 1.14, \quad \frac{k_{40°}}{k_{30°}} = \frac{0.288}{0.271} = 1.06 \quad \text{when } C_{Na_2CO_3} = 0.1875 \text{ N.}$$

$$\frac{k_{30°}}{k_{20°}} = \frac{0.249}{0.221} = 1.13, \quad \frac{k_{40°}}{k_{30°}} = \frac{0.259}{0.249} = 1.04 \quad \text{when } C_{Na_2CO_3} = 0.3750 \text{ N.}$$

$$\frac{k_{30°}}{k_{20°}} = \frac{0.171}{0.150} = 1.14, \quad \frac{k_{40°}}{k_{30°}} = \frac{0.190}{0.171} = 1.11 \quad \text{when } C_{Na_2CO_3} = 0.938 \text{ N.}$$

TABLE 3.

Temp.	$C_{Na_2CO_3}$ normal	k	$k_{calc.}$	Dissolution velocity of oxygen mols per minute.
20°C.	0	0.330	—	8.2×10^{-6}
	0.01875	0.285	0.256	7.1 „
	0.03750	0.264	0.254	6.6 „
	0.0750	0.249	0.249	6.2 „
	0.1875	0.238	0.237	5.9 „
	0.2625	0.227	0.228	5.7 „
	0.3750	0.221	0.215	5.5 „
	0.5630	0.188	0.194	4.7 „
	0.750	0.165	0.172	4.1 „
	0.938	0.150	0.151	3.7 „
	1.125	0.133	0.130	3.3 „
	1.313	0.123	0.108	3.1 „
30°C.	0	0.345	—	8.6 „
	0.1875	0.271	—	6.7 „
	0.3750	0.249	—	6.2 „
	0.938	0.171	—	4.3 „
40°C.	0	0.382	—	9.5 „
	0.1875	0.288	—	7.2 „
	0.3750	0.259	—	6.4 „
	0.938	0.190	—	4.7 „

The Dissolution Velocity of Air. As was expected, the oxidation velocity of sodium sulphite in sodium carbonate solution was independent of its concentration under the condition of this experiment. The result can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into sodium carbonate solution. The dissolution velocity, given in Table 3, is that of oxygen, when air was passed into 40 c.c. of sodium carbonate solution in a test tube (diameter $\fallingdotseq$ 3 cm.) through a glass tube (inside diameter $\fallingdotseq$ 4 mm., outside diameter $\fallingdotseq$ 6 mm.) at the rate of 7.78 litres per hour, and was calculated from the value of k. The dissolution velocity of oxygen into sodium carbonate solution seems to be a little smaller than that into sodium hydroxide solution, obtained in the previous stuty[1].

(1) S. Miyamoto, this journal, **2** (1927), 158; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 192.

Summary.

(1) The oxidation velocity of sodium sulphite in sodium carbonate solution of various concentrations was observed. The oxidation velocity was independent of the concentration of sodium sulphite under the condition of the present experiment, and the velocity constant was expressed as a linear function of the concentration of sodium carbonate approximately, when $C_{Na_2CO_3}$ is greater than about 0.02 normal.

(2) The effect of temperature was small.

(3) The dissolution velocity of oxygen into sodium carbonate solution of various concentrations was obtained indirectly.

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THE SYSTEMS HYDROGEN CHLORIDE—ETHYL ETHER AND HYDROGEN CHLORIDE—ACETONE.

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In 1904, Archibald and McIntosh[1] published the results of an investigation of the compounds produced by the addition of the halogen hydrides to organic substances containing oxygen. They isolated a compound of hydrogen chloride and ether, melting at $-92°$, which had the composition $C_4H_{10}O$–5HCl. This ratio was fixed by two methods. The liquefied acid was "titrated" with ether at the same temperature, and a point was found, corresponding to the ratio of five molecules to one, where the further addition of ether developed very little heat, while before that amount of ether was added, any addition occasioned a considerable heat evolution. By a second method, in which a serious error could hardly be made, the compound was separated, dried at low temperature and analysed. The results showed that the compound corresponded closely to the formula $C_4H_{10}O$–5HCl.

Maass and McIntosh[2] investigated the system ether—hydrogen chloride. They found that the three compounds $C_4H_{10}O$–HCl, 2HCl and 5HCl

(1) *J. Chem. Soc.*, **85** (1904), 919.
(2) *J. Am. Chem. Soc.*, **35** (1913), 535.

existed, so that this system was more complicated than that of the methyl ether and acid, examined by them and by Baume[1]. In 1926 Hirai[2] repeated this work, and concluded that but one compound, $C_4H_{10}O$–2HCl, was formed. As these oxonium compounds have a new interest on account of the development of the electron theory of valence, I have re-examined certain parts of this system. The results show the formation of three compounds mentioned above.

Materials and Apparatus. The ether and acetone were purified and dried by sodium and calcium chloride, respectively. The hydrogen chloride was made by the action of strong sulphuric acid on hydrochloric acid. It was dried by sulphuric acid and phosphoric anhydride.

The apparatus is shown in the sketch. It consisted of a double-walled freezing-point tube, closed by a rubber stopper. This contained a magnetic stirrer and a resistance thermometer. Two glass tubes passed through the stopper; one reaching to the bottom served to introduce the gaseous acid. The solutions were made by weight, all weighings being made at low temperature. We have shown in previous papers that this can be done to 0.1 per cent.

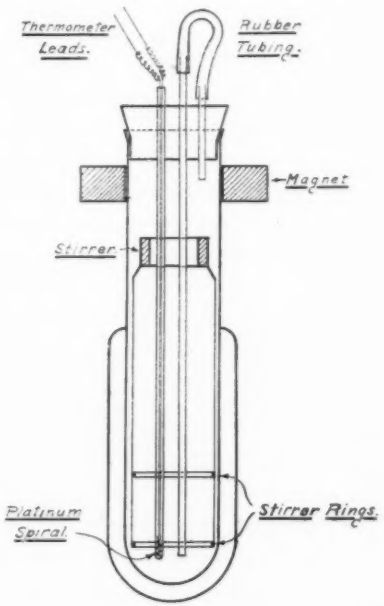

Fig. 1.

A Heraeus platinum-quartz thermometer with a resistance of 25.031 ohms and a Leeds and Northrup bridge were used. The thermometer was tested at the carbon dioxide temperature, at the freezing temperature of acetone (−94.6°), and at the temperature of boiling oxygen. Immediately before or after each series of measurements its resistance at −94.6° or −78.5° was determined.

The solutions were cooled by a bath of carbon dioxide and ether boiling under reduced pressure. It was an easy matter to keep the temperature of the bath within a few degrees of the freezing-point of the solution.

(1) *Arch. Science physiques*, **33** (1912), 415.
(2) This journal, **1** (1926), 123.

TABLE 1.

Experiment	Mols. per cent. Acid.	Freezing-point.	Experiment	Mols. per cent. Acid.	Freezing-point.
1.	42.5	−102.9°	5.	67.6	−83.2°
	47.3	−100.0		70.0	−84.8
	56.5	−100.4			
			6.	80.5	−99.6
2.	53.2	− 98.9		83.6	−92.9
				85.0	−94.2
3.	50.0	− 98.6			
	68.6	− 83.2	7.	81.5	−96.2
				85.0	−94.2
4.	46.7	−101.3			
	54.2	− 97.9	8.	53.7	−99.5
	65.9	− 82.0		67.6	−82.8
	68.6	− 83.2			
	71.6	− 97.6	9.	66.4	−82.0
5.	50.6	− 99.7	10	84.5	−92.6

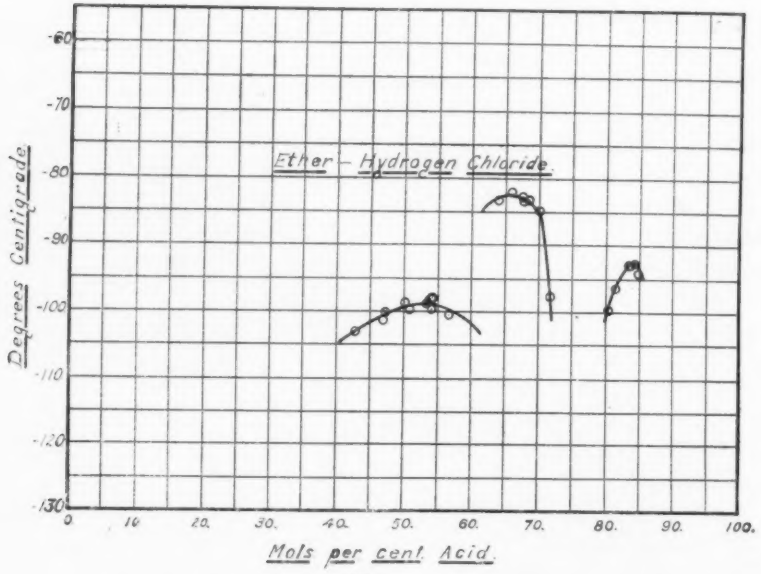

Fig. 2.

The results are shown in Table 1 and on the curve, and indicate the formation of the three compounds found by Maass and McIntosh. The

general form of the curves is the same in the two investigations, but the individual points differ rather widely. From the irregularities in my results an experimental error of about two degrees may be assumed.

The difference in our results is due, I think, to Hirai's failure to realize the difficulty of precipitating compounds from the supercooled liquids. Maass and McIntosh[1] say: "Avoiding too vigorous agitation it is quite possible to maintain the ethers and alcohols in liquefied hydrochloric acid as solutions many degrees below their real freezing-points. The phenomenon of supercooling is particularly well seen in all these oxonium compounds"; and I have repeatedly kept these mixtures at ten degrees below their true freezing-points for five hours at a time, agitating meanwhile with the magnetic stirrer, without precipitation taking place.

It is possible, however, to bring about crystallisation at any temperature below the freezing-point by "inoculating" the solution with a minute amount of the ether-hydrogen chloride or bromide complex introduced by means of a capillary tube. The crystals of the latter are made up of a mixture of $C_4H_{10}O$–HBr and $C_4H_{10}O$–2HBr,[2] and bring about a separation of the one and two hydrogen chloride salts, with a consequent rise in temperature, so that determinations can be made with any desired degree of accuracy. These salts have no influence on the precipitation of the 5HCl compound; that must be brought about by vigorous stirring and low temperature.

The System Acetone—Hydrogen Chloride. Archibald and McIntosh made and analysed a compound containing two molecules of acetone to five of acid. The examination of this system by Hirai yielded only one compound, C_3H_6O–HCl. I have therefore determined a few points on the freezing-point curve, and these show that both compou ds are formed. The results are given in Table 2 and are shown on the cu They are in fair agreement with Hirai's up to sixty mols. per cent. aci

TABLE 2.

Mols. per cent. Acid.	Freezing-point.	Mols. per cent. Acid.	Freezing-point.
36.5	−91.5°	69.7	−81.2°
47.1	−76.9	71.7	−80.8
54.0	−78.0	74.3	−85.3
57.7	−84.6	53.8	−78.0
63.2	−94.6		

(1) *J. Am. Chem. Soc.*, loc. cit.

(2) McIntosh, ibid., **33** (1911), 71; Maass and McIntosh, ibid., **34** (1912), 1273.

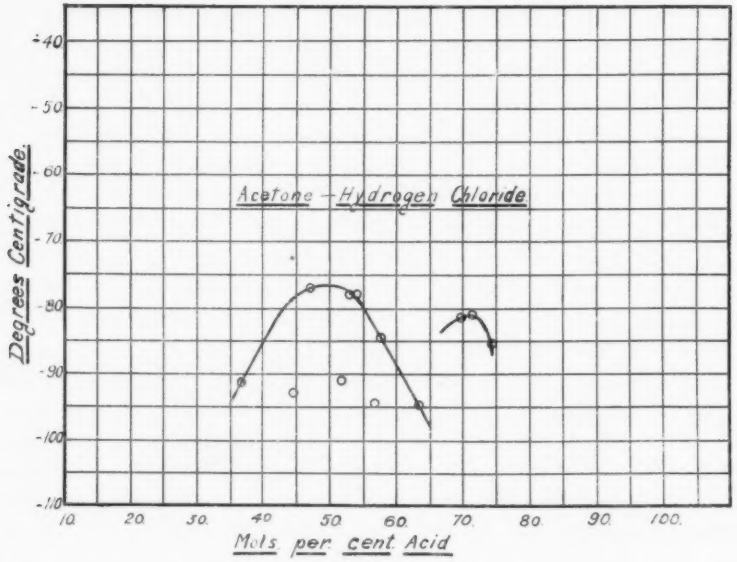

Fig. 3.

What has been said of the ether-hydrogen chloride system applies with equal force to the acetone one. The separation of the first compound takes place on the addition of the acetone-hydrochloric or acetone-hydrobromic complex ; the other compound is not precipitated in this way ; it is formed by cooling the solution and stirring.

The freezing-point (−79°) given by Hirai for his compound is too low. I have kept the solid crystallized from 50.1 mols. per cent. acid at −78.5° for 20 hours without melting taking place.

On the diagram three points inside the curve are shown. These points were obtained when a chalky precipitate, quite different in appearance from either of the two compounds, separated. On re-melting and repeating the observation the result fell on the curve. This may mean a new compound which separates from the solution as does the heptahydrate of sodium sulphate from a supersaturated solution of the decahydrate when the system is cooled to a fairly low temperature.

Finally, an acetone-hydrogen chloride solution containing for more than sixty mols. per cent. acid does not become viscous if kept only a degree or two below its true freezing-point. If cooled to a low temperature it naturally forms a glass.

September, 1927. Dalhousie University,
Halifax, Canada.